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DEVELOPING CURE KINETICS MODELS FOR INTERLEAF PARTICLE TOUGHENED EPOXIES

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ABSTRACT

In this study, we investigated the cure kinetics behaviour of the commercial Hexply® M21 thermoplastic interleaf epoxy resin system. Dynamic, isothermal, and cure interrupted modulated differential scanning calorimetry (mDSC) tests were used to measure the heat flow of the system, and semi-empirical models were fitted to the data. The cure kinetics model describes the cure rate satisfactorily, under both dynamic heating and isothermal conditions. The glass transition temperature was described using the DiBenedetto equation and showed that heating rate can influence formation of the network; therefore cure schedule must be controlled carefully during processing.

1. INTRODUCTION

The highly-crosslinked structure of thermoset materials leads to a low fracture toughness of the cured matrix. Blending amorphous thermoplastic polymers, such as PEI – poly(ether imide), PES – poly(ether sulfone), or PSF – polysulfones, into the thermosetting matrix can result in a cured material with much higher toughness, and perhaps more importantly, a higher elastic modulus during processing to increase viscosity and reduce flow defects [1]. The thermoplastic phase is usually introduced into the thermoset precursors at high temperature. The initial homogeneous mixture undergoes reaction-induced phase separation during cure to produce a thermoset matrix with thermoplastic-rich particles [1]. The average diameter of the precipitated thermoplastic particles is typically sub-micron, with rare instances of large particles approaching 2.5 μm [2]. Given that these particles are much smaller than the diameter of carbon fibre filaments, they can precipitate uniformly through the thickness of fibre reinforced laminates.

An alternative blending approach may involve dispersing preformed semi-crystalline thermoplastic particles, such as PA – polyamide or PBT – poly butylene terephthalate, into the thermoset precursors [1]. Using this approach, the thermoset matrix and thermoplastic particles should remain heterogeneous during cure. Modifications in the thermoset cure kinetics may be observed during polymerisation if the thermoplastic reactive groups participate in the reaction or if non-reactive thermoplastics act as a cure diluent [1]. Introducing preformed thermoplastic

modifiers as core-shell particles may avoid some of the adverse consequences from cure schedule variations on the resulting morphology and properties of the phase separating blends [2].

Regardless of the mixing route chosen, the objective of thermoplastic modifiers is to improve the fracture toughness of the thermoset matrix without compromising the glass transition temperature (T_g) or elastic modulus. By increasing the critical stress intensity factor of the (K_{IC}) of the blended matrix, the radius of the plastic zone ahead of the crack tip now becomes much larger than that interlaminar spacing between plies [3]. In-order to fully exploit the higher K_{IC}, the plies need to be spaced further apart for the strain-energy release rate (G_{IC}) to increase. Increasing the interlaminar spacing between plies can be accomplished by either introducing a same-self resin interlayer [4] or using preformed thermoplastic particles to create the interlayer [5]. It remains to be seen whether the particles improve toughness by forcing the crack path through the particles, thereby absorbing more energy in the fracture process, or simply act as a spacer to keep the damage zone ahead of the crack tip in the interlaminar region.

Introducing an interlayer region with preformed particles between plies to improve cured laminate toughness may present some unique processing challenges over traditional reaction-induced phase separating systems. A lower through-thickness thermal conductivity is expected, which can lead to more severe temperature overshoots in thick composite sections. Additives may be used to improve the chemical adhesion between the thermoplastic particles and thermoset matrix [1], and some studies suggest that volatiles are released from these additives during cure [6]. An alternative approach to improve adhesion may be to functionalise the thermoplastic particle chain ends [1], which can react with the epoxy groups once melted [7]. These factors, combined with microstructure development during phase separation may influence the final cured properties of interlayer toughened prepreg systems if the cure schedule is not carefully controlled [8].

The main objective of this study was to develop a cure kinetics model to describe the reaction kinetics of a preformed thermoplastic particle toughened epoxy system. Secondary objectives included identifying whether cure path dependencies, such as heating rates, would influence network formation. We also wanted to identify the claims from other studies that suggested DSC experiments were not suitable for third generation (particle interleaf) prepreg epoxy systems because of test scatter [6].

2. EXPERIMENTATION

2.1 Material

A commercially available thermoplastic interleaf particle epoxy system, Hexply® M21, was chosen for this study. This material system has di-, tri-, and tetra-functional epoxy groups and a diaminodiphenyl sulfone (DDS) curing agent [9]. The loading and composition of the preformed particles is unknown and was not investigated. The existence of reaction-induced phase separating amorphous thermoplastics is also unknown and was not investigated. The recommended cure schedule for M21 is a single step cure at 180 °C for 2 h with part heating rates of 1 to 2 °C/min [10].

2.2 Thermal Gravimetric Analysis (TGA)

The thermal stability of the material was investigated using a TA Instruments Q500 TGA at the UK National Composites Centre. The balance was calibrated using reference masses and the temperature was calibrated using Curie materials. Four dynamic heating ramps were performed at rates of 1, 2, 5, and 10 °C/min in a nitrogen atmosphere.

2.3 Modulated Differential Scanning Calorimetry (mDSC)

Dynamic, isothermal, and interrupted dynamic and isothermal mDSC experiments were performed using the approach outlined by Dykeman [8]. A TA Instruments Q2000 at the UK National Composites Centre was used to perform the calorimetry. The dynamic experiments were used to calculate the total heat of reaction and the cure behaviour at different heating rates, whereas the isothermal runs were carried out to investigate the effect of different temperatures on the cure behaviour of the material. In the dynamic tests the samples were cooled to ambient to measure the final T_g after testing and the isothermal runs were quenched to ambient before re-scanning in dynamic mode at 5 ± 1.25 °C to 300 °C to measure the T_g after the isotherm and the final T_g of the sample. The interrupted experiments were used to identify whether a cure path dependency on network formation was measurable by calorimetry. The test matrix is presented in Table 1.

Table 1. mDSC Test Matrix

	Modulation per minute (± °C)	**End temperature (Dyn)**	**Hold time (Iso)**
Dynamic heating rate (°C/min)			
1	0.25	275	
2	0.5	150, 175, 200, 225, 280	
5	1.25	200, 225, 300	
10	2.5	350	
Isothermal hold temperature (°C)			
140	1		600
150	1		15, 30, 60, 90, 120, 150, 200, 500
160	1		400
170	1		300
180	1		7.5, 15, 30, 60, 90, 300
190	1		200
200	1		200

For the dynamic experiments, mDSC was chosen because it can separate the reversible and non-reversible parts of the heat flow signal as shown in Figure 1. The total heat flow signal captures the uncured T_g of the resin, but is unable to separate the cross-linking of the epoxy monomers and the reversible melting of the preformed thermoplastic particles at around 185 °C. Given this, the

non-reversible heat flow signal was used to calculate the dynamic heat of reaction and eventually the cure rate in this study.

MDSC was also chosen for the isothermal experiments because both the heat flow out of the material and heat capacity evolution can be captured from a single experiment, as shown in Figure 2. If a full thermal model is needed in the future the heat capacity can be modelled from these single mDSC experiments.

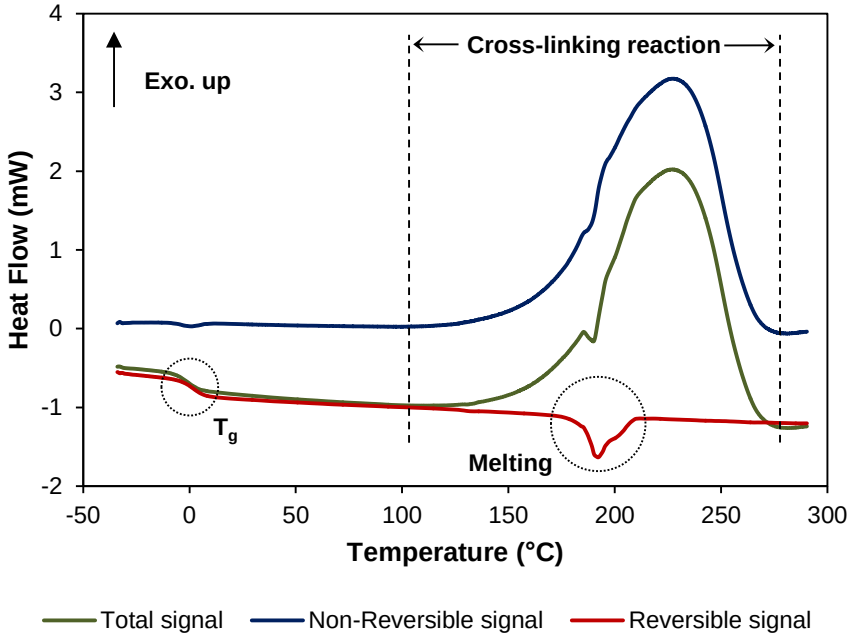

Figure 1. Dynamic mDSC scan at 5 °C/min with a ±1.25 °C modulation per minute.

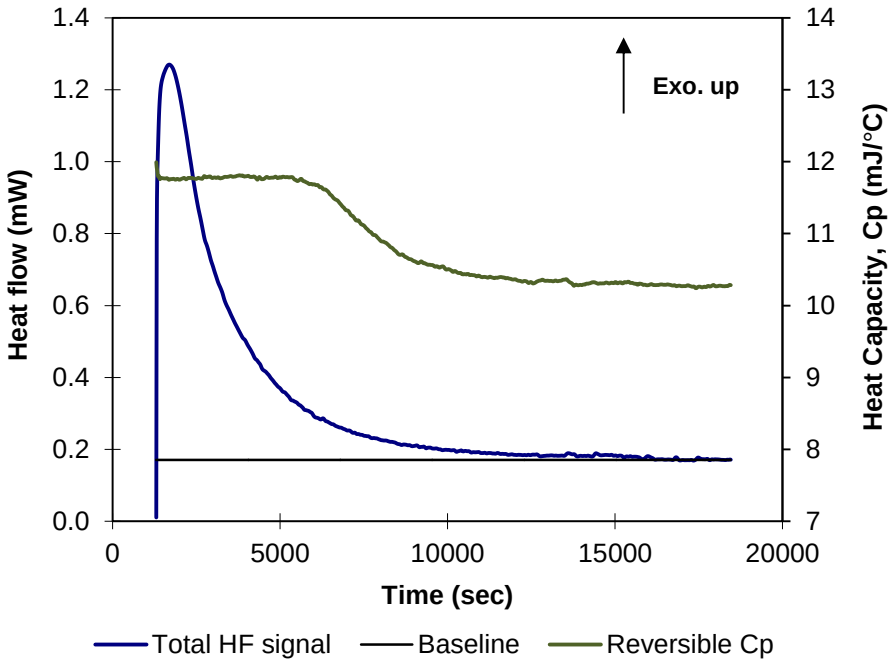

Figure 2. Isothermal mDSC scan at 180 °C with a ±1 °C modulation per minute.

2.4 Baseline

The choice of baseline will influence the total heat of reaction, and the eventual cure rate and degree of cure calculation of the material. Barton [11] has identified the four principle baseline constructions used for epoxy materials, shown in Figure 3. One study has pointed towards no theoretical justification for the implementation of a linear baseline since the heat capacity of the resin is not expected to change in a linear or sigmoidal fashion [13]. Therefore, an iterative baseline can be used to integrate the heat flow versus time during dynamic cure [12,13]. When using an iterative baseline, the resin heat capacity is assumed to be changing gradually from the onset until the completion of the reaction and its value at any intermediate point is considered to be a linear function of the progress of this reaction. Consequently, at the start of the reaction this method yields the initial heat capacity value, whilst at maximum conversion it yields the final heat capacity value [13].

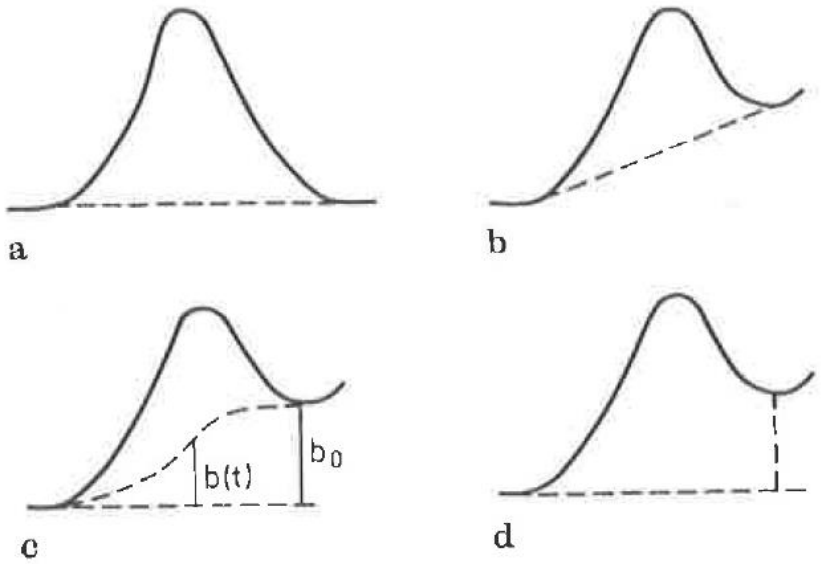

Figure 3. Possible baseline constructions for dynamic DSC tests, from Barton [11]: a) horizontal, b) linear, c) proportional, and d) linear with vertical boundary.

3. RESULTS

3.1 Thermal Stability

The results of the TGA experiments are shown in Figure 4. The material showed a weight change of between 2 to 5% in the dynamic heating rates of 1 to 10 °C/min used in this study. At the isothermal temperatures studied, below 200 °C, a weight change of less than 1% would be expected based on the TGA experiments. The consequence of these results are in relation to the baselines chosen. Given the small weight change during the isothermal experiments, the horizontal baseline seems like a suitable choice. Variations in the dynamic total heat of reaction reported by Dykeman [8] were attributed to possible vitrification in slow heating rates and degradation not entirely removed by the chosen linear baseline with a vertical boundary to capture degradation. The influence of thermal degradation on baseline selection will need to be considered in this study since the higher heating rate mDSC experiments will exceed the recommended 180 °C processing temperature, and will likely degrade the matrix during testing.

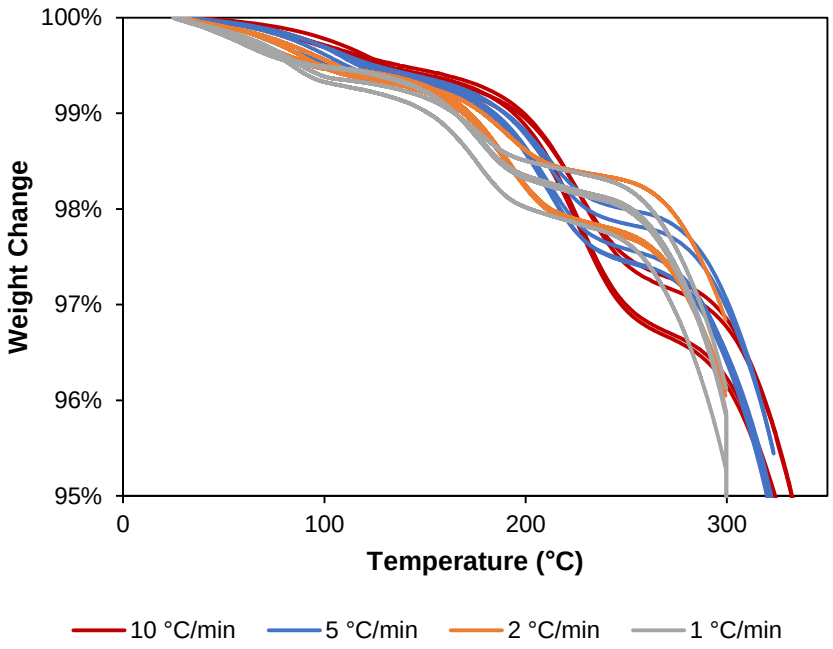

Figure 4. TGA test results.

3.2 Cure Kinetics Model Development

The degree of cure, α, at any time t, can be evaluated using the following expression:

$$\alpha = \frac{\int_{t_1}^{t_2} \frac{H}{dt} dt}{H_T} \tag{1}$$

Here t_1 and t_2 is the time the reaction started and completed respectively, whilst H is the heat released at any time, t, and H_T is the total heat of reaction. The total heat of reaction H_T is calculated by integrating the total area enclosed by the thermogram (such as Figure 1) during dynamic cure.

$$H_T = \int_{t_1}^{t_2} \frac{H}{dt} dt \tag{2}$$

In the case of dynamic cure, the resin absorbs or emits heat, at a rate depending on its heat capacity evolution. Therefore, an appropriate baseline should be chosen being able to reflect this phenomenon in order to carry out the integration shown in Eqns. (1) and (2). In common practice a linear or sigmoidal baseline is used (see Figure 3). A linear baseline was used as a first attempt to calculate the total heat of reaction, and this produced an average value of 430 J/g with a coefficient of variation of 11.3%. Surprisingly, the total heat of reaction also decreased with increasing heating rate, as shown in Figure 5. Re-integrating the dynamic heating scans using an iterative baseline generated a mean total heat of reaction value of 415 J/g with a coefficient of variation of 2.8% and, as can be seen in Figure 5, fairly uniform values across the range of heating rates studied. In the case of isothermal scans, a horizontal baseline was implemented as shown in

Figure 2, whilst the mean value of the total heat of reaction calculated during the dynamic scans was used to perform the integration described by Eq. (2).

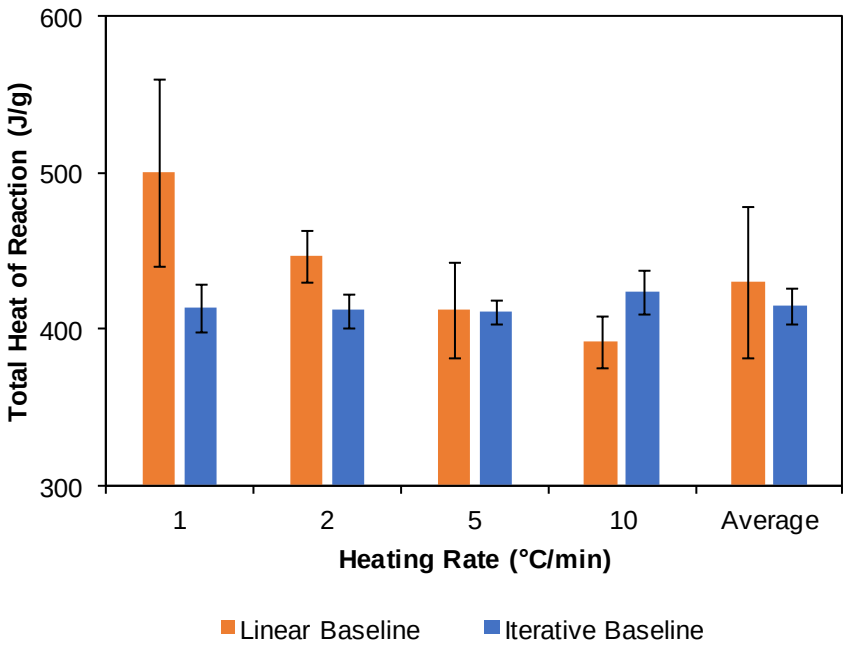

Figure 5. Total heat of reactions calculated using linear and iterative baselines for the dynamic mDSC tests. Error bars represent ± one standard deviation.

The modelling methodology adopted here was first to develop a cure kinetics model in the case of isothermal cure leading to a first approximation of the kinetic parameters. This model was then fitted to the dynamic scans for an accurate estimation of the cure kinetics parameters. The model applied to the isothermal cure was an autocatalytic model described by the following equation [14]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{3}$$

where $\frac{d\alpha}{dt}$ is the cure reaction rate, m and n are reaction orders, and k_1, k_2 are reaction rate constants following an Arrhenius temperature dependence:

$$k_i = A_i e^{\left(\frac{-E_i}{RT}\right)}, i = 1,2 \tag{4}$$

where E_1, E_2 are activation energies, and A_1, A_2 are pre-exponential Arrhenius constants. A first approximation of k_1 was determined using the initial reaction rate values as proposed in [14], whereas the remaining parameters of Eq. (3) were estimated using Eq. (4) [15]. To calculate these values, the isothermal scans were used to plot of the left hand side of Eq. (4) versus $ln\alpha$, which yields a straight line with intercept $\ln k_2$ and slope m [15]:

$$\ln\left(\frac{\frac{d\alpha}{dt}}{(1-\alpha)^n} - k_1\right) = \ln k_2 + m\, ln\alpha \tag{5}$$

The cure kinetics model developed using solely the isothermal scans presented a poor fit to the dynamic cure response; this was most likely due to the narrow temperature range for which the model parameters were evaluated. Therefore, a re-evaluation of the cure kinetics parameters described by Eq. (3) was required. Eq. (3) was modified to Eq. (6) in order to capture the cure behaviour at the final stages of cure more accurately as described in [15].

$$\frac{d\alpha}{dt} = k_1(1-\alpha)^{n_1} + k_2\alpha^m(1-\alpha)^{n_2} \tag{6}$$

The cure kinetics model described by Eq. (6) was fitted to the dynamic runs using the generalised reduced gradient non-linear optimization method implemented in Microsoft Excel [16]. Table 2 summarises the cure kinetics parameters identified using this modelling methodology. These parameters are fit to the isothermal and dynamic mDSC scans in Figure 6 and Figure 7, respectively. These figures show there is a very good agreement between the cure kinetics model and experimental data for both isothermal and dynamic scans, implying that the proposed cure kinetics model is able to replicate the cure behaviour of the HexPly® M21 resin system considered in this study.

Table 2. Cure Kinetics Parameters

Kinetic parameter	**Value**
A_1	420615 [1/s]
E_1	78890 [J/mol]
A_1	57440 [1/s]
k_1	68978 [J/mol]
m	0.61
n_1	0.8
n_2	3.22

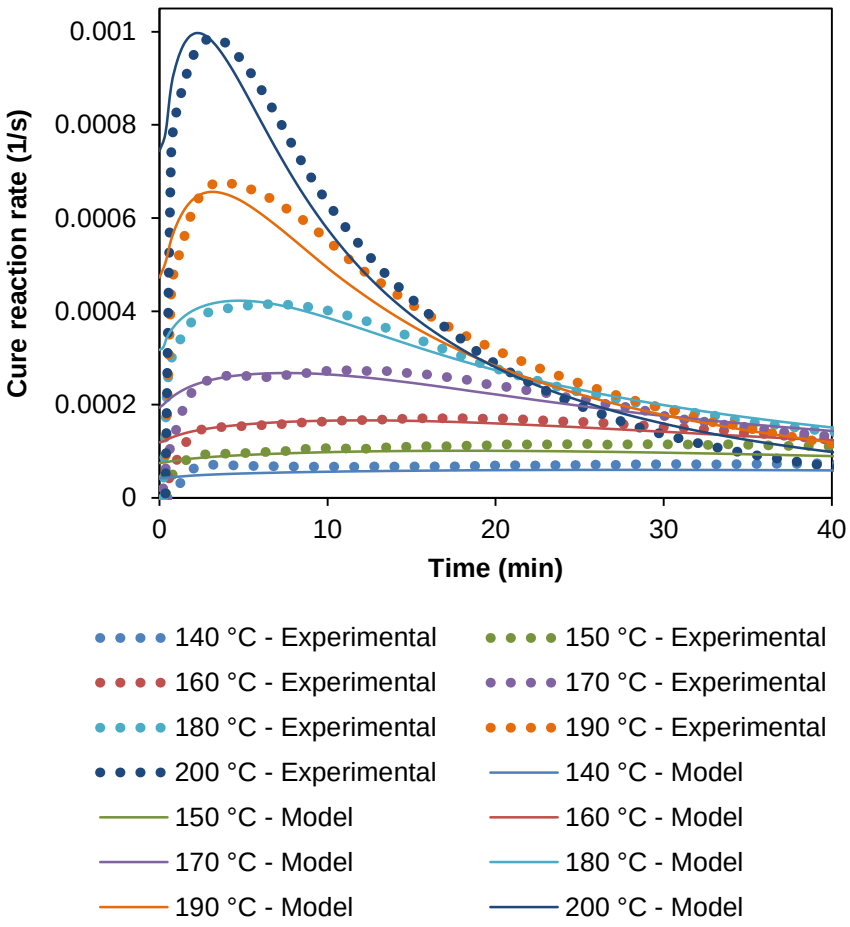

Figure 6. Cure reaction rate evolution as a function of time during isothermal tests.

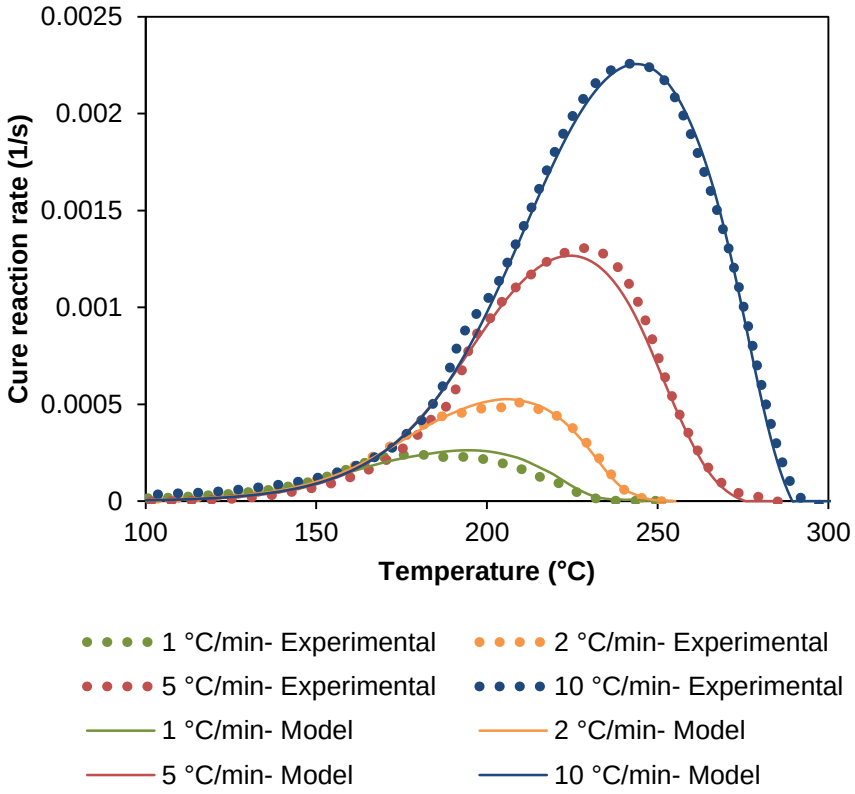

Figure 7. Cure reaction rate evolution as a function of temperature during dynamic tests.

3.3 Glass Transition Temperature

The evolution of the glass transition temperature, T_g, with degree of cure is shown in Figure 8. These results were obtained from the interrupted mDSC tests presented in Table 1. The network formation in the interrupted experiments heated at 5°C/min does not appear to follow the same network formation behaviour as in those interrupted at 2 °C/min or the interrupted isotherms at 150 and 180 °C. Heating the material at 5 °C/min forces the majority of network formation to proceed well above the recommended process temperature of 180 °C. Modification in the reaction rates have been observed in preformed particle toughened materials when the thermoplastic phase is molten while the thermosetting resin is at a low degree of cure [17].

Neglecting the dynamic heating ramps at 5 °C/min, the experiments follow the relationship described by DiBenedetto [18]:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1-(1-\lambda)\alpha} \tag{7}$$

where T_{g0} is the uncured glass transition temperature of 1.5°C, $T_{g\infty}$ is the ultimate glass transition temperature of 194°C, α is the instantaneous degree of cure, and λ is a fitting parameter that was found to best approximate the experimental data at a value of 0.67 using a weighted least squares solution.

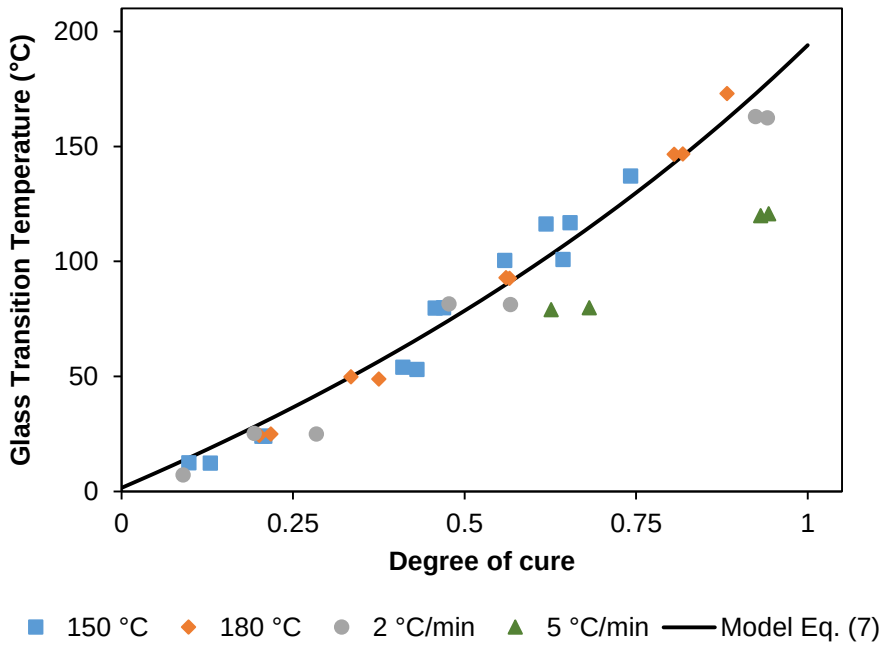

Figure 8. Evolution of the glass transition temperature with degree of cure.

4. CONCLUSIONS

The cure behaviour of a preformed particle interleaf toughened epoxy matrix resin system was studied by modulated Differential Scanning Calorimetry (mDSC) in isothermal and dynamic heating conditions. An iterative baseline was needed to reduce variability in the total heat of reaction calculations measured when using a linear baseline. The chosen model accurately describes the kinetic behaviour in both dynamic and isothermal heating conditions, and serves as a starting point to model the full thermal behaviour during processing.

The overall cure behaviour of the preformed thermoplastic particle toughened epoxy system appears to follow the traditional reaction kinetics of epoxy resins. However, heating at higher temperature rise rates, and processing the material well above the recommended cure temperature, showed deviation from the classical glass transition temperature evolution. Interrupted mDSC tests with heating rates at 5 °C /min lead to presumed differences in network formation that were not observed at 2 °C /min. Further experiments are required to identify the heating rate threshold where network formation is unaffected.

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